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THERMOCHEMICAL AND KINETIC CONSIDERATION IN DIAMOND GROWTH

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Thermochemical and Kinetic Considerations in Diamond Growth

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Abstract

Considerations important to the modeling of the diamond growth process include the question of what surface structures may exist during the growth process and how these structures may be determine or be determined by the composition of the gas phase adjacent to the surface. The simple truncated lattice structures of the three low index surfaces are reviewed and the steric problem inherent to the hydrogenated unreconstructed (100) surface is illustrated. It is proposed that the <110> zone axis is the ghest growth rate direction as this is the dominant texture seen in many experiments and that a model for diamond growth along this axis should therefore be of great interest. The assumptions inherent in much modeling are illustrated through the calculation of the mole fraction product of surface reactive sites and the methyl radical, giving a value of ~10^{-7}. If a methyl radical mole fraction of 10^{-3} to 10^{-4} is assumed then the mole fraction of reactive sites at the diamond surface would have to be approximately 10^{-4} to 10^{-3}. Included in these assumptions is that the rate limiting process is the addition of carbon at the growth surface, that the diamond surface can be treated in effect as a large hydrocarbon, and that the only reactions of importance are those that would also be observed for simple hydrocarbon species in the gas phase. The last of these assumptions needs to be carefully considered in light of the fact that an activated diamond surface is known to catalyze the H_2/D_2 exchange reaction at low temperatures.

Introduction

Numerous models have been offered to rationalize the growth of diamond with some focusing on various charged species [1-3], others suggesting acetylene as the dominant growth species [4-6], and still others focusing on various reactive radicals, ranging from atomic carbon [7] to the methyl radical [8-12]. The suggestion that neutral radical chemistry plays an important role has a long history, beginning with the early suggestion by Eversole [8] that "...either methane or compounds that decompose to methane or methyl radicals are needed." Mania et al. [9] also suggested that the methyl radical was important with the logic that species having sp^3 hybridized radicals would more easily lead to diamond than sp^2 hybridized radicals or molecules. These were thought to more likely contribute to the formation of graphite. The logic appears flawed in that spectroscopic study has shown that the methyl radical in the gas phase has planar D_3h symmetry, and thus in its ground state, is sp^2 hybridized with the unpaired electron in the unhybridized p orbital lying along the three fold axis [10]. Nevertheless the idea that the methyl radical is an important precursor to diamond growth led Hirose and Tersawa [11] to test numerous feed gases in hot filament CVD with the conclusion that it plays an important role and Harris [12] proposed a reaction mechanism for the unreconstructed (100) diamond surface based upon the idea that the methyl radical is the dominant additive specie. From modeling and characterization of the gas phase, various researchers have reached the conclusion that only acetylene, methane or the methyl radical exist in high enough concentrations to account for the observed growth rates in hot filament CVD [13-15]. The technological importance of the growth chemistry relates to a wide variety of problems and questions. Among these are: What directions should be taken to improve both growth rate and crystal quality? What are the critical parameters in designing and building large scale reactors? Can reactor modeling be used to help design larger and more efficient reactors? Are there new or unexplored methods that might be successful?

Experiments in different laboratories have been reported comparing the efficacy of acetylene and methane in the feed gas to each other. Martin and Hill [16,17] used a remote plasma technique to dissociate hydrogen and fed methane downstream of the plasma. They reached the conclusion that the additive specie was short lived and probably the methyl radical. In the work reported by Chu et al. [18,19] C^{13} enriched gases were fed locally to a substrate and diamond grown using the hot filament method. The proportions of C^{13} and C^{12} found in the diamond were compared to the proportions used in the methane and acetylene feed gases with the conclusion that although the best fit to the data would postulate some acetylene activity, the dominant source of carbon was from methane. In a third set of experiments Yarbrough, Tankala and DebRoy [20] similarly used a local feed to the substrate in a hot filament system and compared the growth rates and uniformity of deposition using acetylene or methane as the source of carbon. In the latter work it was found that although diamond could be

grown using acetylene, methane was a much more efficient feed gas. Furthermore it was found that the uniformity of deposition was dramatically affected by the use of methane and relatively unaffected by the use of acetylene. In all these experiments the conclusion was reached that the dominant mechanism was likely one based on a reactive specie more readily derived from methane than from acetylene. Thus both from experiment and by thermochemical modeling, the methyl radical appears the dominant additive specie in hot filament CVD.

The Critical Role of the Solid Surface

Ultimately any mechanism for the synthesis of a solid from either a gas or liquid must address the interface between the solid and the growth medium, that is the solid surface and fluid immediately adjacent to it. Over the past decade many hypotheses have been advanced, not only trying to rationalize diamond growth, but also to suggest the species and parameters critical to the process by which it is nucleated and grown. All these suffer from major uncertainties and a critical one is that all postulate a structure for the solid surface in reaction. Very little is known about the chemistry and physics of the growth surface and very little is known about the elemental reactions at that surface. Compounding this is the need not only to understand nucleation and growth, but also to be able to identify the parameters controlling the creation of defects. Thus a complete growth mechanism must not only describe how the important gas phase species are generated, and carbon is added to the growing crystal, but also how the surface is activated and how the added carbon becomes incorporated into the diamond lattice.

To illustrate the problem, prominently discussed among these models and approaches are those based on the detailed chemical kinetic modeling of elementary reactions [4-6,12,14,21]. This is potentially a powerful technique in that, in principal, an unlimited number of potentially important elementary processes can be included, and software is available linking chemical kinetics with transport phenomena [22]. Through a sensitivity analysis of the output data those reactions found to be unimportant can then, in principal, be eliminated and the reaction set should converge on the important reactions. In many of these efforts, relevant reactions and rate constants have been adopted from gas phase hydrocarbon chemistry, notably the extensive literature developed over the past two to three decades in modeling combustion phenomena. The diamond surface has been treated essentially as a large aliphatic hydrocarbon and the reaction chemistry at its surface described accordingly. This is at best an approximation as there are numerous steric and electronic effects at the solid surface whose importance are unknown, and about which there has been much speculation and debate. For example, Grot [23] has shown that the hydrogenated diamond (100) surface obtained using plasma assisted CVD is electrically active and that to prepare an ohmic contact, it must be chemically treated. Simple aliphatic hydrocarbons are insulating and this surface at least may well not have the simple structure and chemical properties often pictured for it.

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The truncated lattice structures of the three principal low index surfaces of diamond are shown in Figures 1 through 3. In all three cases it is widely assumed that these surfaces are hydrogen terminated and the small unshaded atoms are hydrogen atoms bonded to the surface carbon atoms (large unshaded atoms) to form simple C-H groups at the surface. The most thoroughly studied surface of diamond has been the (111), pictured in Figure 1. With hydrogen satisfying the "dangling bonds" created by simple truncation of the lattice the position of the surface carbon atoms is believed the same as in the bulk. However if the surface is heated to high temperature (~950° C) at low pressures (<<1 Torr) this hydrogen is desorbed and the surface reconstructs to a π bonded chain or possibly a "warped" benzene ring structure [24-26].

The diamond (100) surface has also been studied but nevertheless its structure remains a subject of considerable debate. The first step, common to numerous mechanisms, is the activation of a surface site by atomic hydrogen abstraction, which might be written as:
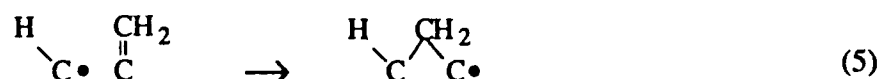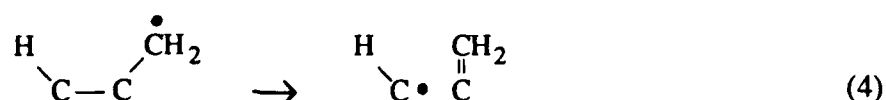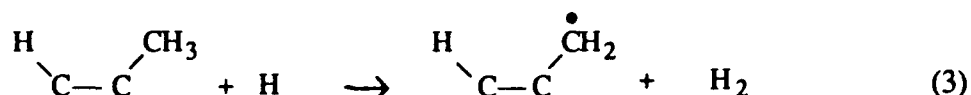
$$C_{(s)}H + H\bullet \rightarrow C_{(s)}\bullet + H_2 \tag{1}$$

where the symbol $C_{(s)}$ denotes a carbon atom at the surface. This step is followed by the addition of a methyl radical to the surface radical which would be written as:

$$C_{(s)}\bullet + CH_3\bullet \rightarrow C_{(s)}CH_3 \tag{2}$$

The major difficulty for the unreconstructed diamond (100) is the steric interference likely between the methyl radical and the neighboring hydrogen atom or in general between neighboring hydrogen atoms on an unreconstructed (100) surface. This problem is illustrated in Figure 2 which shows the dihydrogen terminated and unreconstructed diamond (100). Using bond lengths of 1.54 Å for the carbon-carbon bonds and 1.10 Å for the carbon-hydrogen bonds, with perfect tetrahedral bond angles of 109.5°, one calculates an internuclear hydrogen-hydrogen spacing on this surface of ~0.77 Å, or nearly the same as that in the H_2 molecule, 0.74 Å. As this is a non-bonding interaction, very significant steric repulsion is expected, leading presumably to significant deviation from the model structure. The difficulty is even more severe obviously if one of these hydrogens is replaced by a methyl group. Significant bond angle and bond length distortion can occur in a simple model compound, however the simple (100) surface will not permit significant deviation without some reconstruction. An important way of overcoming this objection is to postulate that the simple dihydrogen terminated pictured in Figure 2 doesn't exist and that growth occurs on the 2x1 reconstructed (100) surface shown in Figure 3. Recent theoretical and experimental work strongly suggests that this is indeed the case [27,28], and that a chemical model for diamond growth on (100) should start with the 2x1 reconstructed surface. This problem has been studied by Garrison and her

co-workers who have proposed a five step mechanism for methyl radical based growth on this surface [29]. The first two steps are the addition of a methyl group to one of the carbons at a dimer through reactions (1) and (2). This is followed by atomic hydrogen abstraction from the methyl group and rearrangement of the resulting methylene radical, incorporating the added carbon into the diamond lattice as illustrated in reactions (3) through (5):

$$
\begin{array}{cc}
\underset{\text{C}-\text{C}}{\overset{\text{H} \qquad \text{CH}_3}{}} + \text{H} & \longrightarrow & \underset{\text{C}-\text{C}}{\overset{\text{H} \qquad \overset{\bullet}{\text{CH}}_2}{}} + \text{H}_2
\end{array} \qquad (3)
$$

$$
\underset{\text{C}-\text{C}}{\overset{\text{H} \qquad \overset{\bullet}{\text{CH}}_2}{}} \longrightarrow \underset{\text{C} \bullet \; \text{C}}{\overset{\text{H} \qquad \text{CH}_2}{}} \qquad (4)
$$

$$
\underset{\text{C} \bullet \; \text{C}}{\overset{\text{H} \qquad \text{CH}_2}{}} \longrightarrow \underset{\text{C} \quad \text{C} \bullet}{\overset{\text{H} \quad \text{CH}_2}{}} \qquad (5)
$$

This mechanism is attractive in that it provides for addition to the 2x1 surface, overcoming the steric problem, and furthermore provides a means of incorporating the added carbon into the diamond surface structure without requiring the formation of a biradical. Another low index surface of great interest is the (110) as both theoretical and experimental results suggest the <110> as the highest growth rate axis.

It has been known for many years that CVD, and other uniaxially grown, crystalline materials often exhibit a fiber-like crystallographic texture [30]. The simplest model is that as individual crystals grow from randomly oriented, discrete nucleation sites to interference and film formation, grain boundaries are formed between them and their lateral expansion is prevented by the presence of neighboring crystals. If surface and bulk diffusion are relatively slow the crystals grow dominantly along the axis normal to the plane of the layer. If growth is not spherically symmetric and crystal growth occurs at higher velocities in some crystallographic directions than in others, then some nuclei will be favorably oriented and many others more or less unfavorably oriented. As growth continues, those with favorable orientations grow more rapidly, extending above and expanding laterally at the expense of those less favorably oriented. This leads to a fiber-like morphology, well documented for CVD diamond in the microstructural studies of Sato, Hata and Kamo [31]. As the morphology evolves it will begin to exhibit the crystallographic texture of its dominant growth axis and this has been modeled in two dimensions for CVD diamond by Wild et al. [32]. Thus, in general, no special property need exist to rationalize the development of crystallographic texture other than the idea that

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crystals grow more rapidly along some axes than along others. The textures or zone axes commonly seen in relatively thick layers are the <110> [32-34] or a <100> [35]. In a careful x-ray analysis of a <100> texture layer Sprecht, Clausing and Heatherly [35] found that the dominant growth axis was a vicinal axis near <100>. This suggests that growth occurred, not along a true <100> zone axis, but possibly along two or more axes whose vector sum leads to an axis near <100>. The suggestion that the <110> is the highest growth rate axis is also supported by Geis's [36] experiments in undoped homoepitaxial growth where the order found was (110) > (111) ≥ (100). Interestingly boron doping appeared to dramatically effect the growth rates obtained, however the <110> remained the highest growth rate axis. It follows from this model that many layers and films may exhibit a near random crystallographic texture if they are thin relative to the mean free distance between nuclei, if conditions are such that random renucleation readily occurs, or importantly if their growth rate is limited by mass transport in the gas phase.

There are at least two other motivations for taking the (110) surface as the dominant growth surface in most experiments. Previous calculations using a group additivity approach suggested the (110) surface should have the lowest enthalpy of formation [37]. If the entropies of the hydrogenated low index surfaces are all relatively small, or nearly equal, then their chemical potentials are determined primarily by their respective enthalpies. Linear non-equilibrium thermodynamics requires that the rate of carbon addition be balanced with the transport of reactive species to the surface. If the addition reaction is not transport limited then the rate of addition at these surfaces should vary as the chemical potential difference between the surface and gas phase reactants. This difference would be largest for the (110) surface, suggesting the <110> zone axis as the largest growth rate axis. Another motivation is that, in the absence of film formation, the crystallographic habit of vapor phase grown diamond in most experiments is cubooctahedral, clearly showing development of both (100) and (111) habit planes. In the simple linear growth of crystals the highest growth rate axes show extinction of the habit planes normal to them. This further suggests the <110> as the highest growth rate axis as it is the (110) habit plane that is missing in cubooctahedral growth. Notably in those cases where a <100> or near <100> growth texture is seen, clearly present are also (100) habit planes or facets at the surface. This apparent violation can be rationalized by arguing that this morphology results not from the <100> being the dominant axis, but rather arises from nearly equal growth velocities along mutually perpendicular <110> and <011> axes, giving a near <100> texture, but not requiring extinction of the (100) facet.

Thermodynamic and kinetic considerations

Non-equilibrium thermodynamics requires, as long as the product of the mean free path with the spatial gradients of temperature, pressure, chemical potential, and other system properties (T, p, μ, etc.) are small relative to their average values, that the fundamental equation of equilibrium

thermodynamics hold for a properly chosen local volume element [38]. That is that:

$$dG = Vdp - SdT + \sum_{\gamma=1}^{c} \mu_\gamma dn_\gamma \qquad (6)$$

where G, V and S are the Gibbs free energy, volume and entropy, respectively, of the local system. The summation is over all the components of the system, c in number, and μ_γ and n_γ are the chemical potential and molar concentration of the γ component respectively. This is known as the local equilibrium assumption or approximation, the principle that with the constraints given above, (6) remains valid for a local volume element of a system where (6) would not be true for the entire system. At a constant local temperature and pressure this requires that

$$dG = \sum_{\gamma=1}^{c} \mu_\gamma dn_\gamma \qquad (7)$$

For a steady state to exist, where dG = 0, this requires that a change in composition due to reaction be balanced by a flux to or from the surface. Hence at pressures greater than ~1 Torr, where the mean free path can be measured in microns, local equilibrium requires that the reactions occurring at the surface balance with the transport of species to or from the surface. For a first order heterogeneous reaction, with a rate constant k, of an gas phase species, i, this gives the balance equation;

$$k [n'_i] = - D_i \text{ grad } n_i \qquad (8)$$

where n'_i denotes the concentration at the solid surface, D_i is its diffusivity and grad n_i is its concentration gradient near the surface. In the limit of one dimensional diffusion with reaction at a solid surface this can be further simplified. If the concentration of the ith component remote from the surface is fixed by an external boundary condition to have some value, n_i°, then (8) can be rewritten as [39]:

$$k [n'_i] = - \beta_i [n^\circ_i - n'_i] \qquad (9)$$

where β_i is a mass transfer coefficient with the units of velocity and the positive flux direction is away from the surface. This simply requires that for a steady state to exist, if the species i is consumed at the surface there must be a balancing flux of that species to the surface to maintain dG=0 and the local concentration of i constant. A solution to (9) requires that the "effective" or overall rate constant for reaction be given by:

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$$k' = \frac{\beta k}{\beta + k} \tag{10}$$

and that the concentration of the reacting gas phase species, i, at the surface be given by:

$$n'_i = \frac{\beta_i}{\beta_i + k} n^0{}_i \tag{11}$$

With reference to equation (10) two limiting cases become apparent. In the first case D or $\beta >> k$ so that $k' \approx k$, the concentration gradient tends to vanish and the rate of reaction at the surface becomes independent of the flux. This is precisely the limit in which the local equilibrium assumption of linear non-equilibrium thermodynamics fails and (6) no longer holds at the solid surface. In the limit that $\beta << k$, $k' \approx \beta$ and the rate of reaction becomes mass transport limited. In this limit the local concentration of the gas phase reactant becomes small, i.e. $n'_i \approx \beta/k$, and will approach the value required at thermostatic equilibrium. The phrase "local equilibrium" has been used in this restricted sense i.e., where the local concentrations must approach their thermostatic equilibrium values [40]. This should not be confused with "local equilibrium" in the thermodynamic sense where for a steady *state system it is only required* that (6) be valid in a local volume element. In most cases the rate constant k is relatively insensitive to pressure while the diffusivity, D, and hence the mass transfer coefficient, β, are inversely proportional to pressure. This introduces a possible pressure dependence with the diamond growth rate becoming increasingly diffusion limited with increasing pressure. An important result is that (7) or (8) requires, if $k > \beta$, that adjacent to the growing diamond surface there also exist a concentration gradient for the reacting species. Thus concentration measurements made of gas phase species in the absence of the diamond surface, or under sampling conditions where the solid surface has little or no effect on the measurements, are misleading. If such measurements are then used to calculate a growth rate using homogeneous rate constants from gas phase chemistry, significant error can result.

Numerous studies have been made of hot filament activated systems and at pressures of 20 to 50 Torr using 1% CH_4 in H_2 growth rates of ~0.5 $\mu m/hr$ are commonly reported[11,41,42]. With the assumption that the surface of interest is the (110), an estimate can be made of the relative mole fractions necessary for this growth rate. If reaction (2) is assumed the limiting reaction, i.e. that the rate of carbon addition is the growth rate of diamond, then its rate should be given by the expression:

$$\text{Growth Rate} = k \, [CH_3] \, [C_{(s)}{}^\bullet]$$

where the bracketed quantities are the local concentrations of these species. Thus to calculate a growth rate based solely on the methyl radical and compare to experiment we need to generate estimates for k, the local concentration of the methyl radical, $[CH_3]$, and the concentration of radical or reactive sites at the diamond surface, $[C_{(s)}\cdot]$. The dimensions of a unit mesh of diamond (110) are given in Figure 4 where two carbon atoms occupy a surface area of 2.52 Å x 3.57 Å or 9.00 x 10^{-16} cm^2. Multiplying this by Avogadro's number, dividing by 2 and inverting gives that the concentration of carbon at the hydrogenated (unreconstructed) diamond (110) surface is 3.69 x 10^{-9} mols cm^{-2}. Thus $[C_{(s)}\cdot]$ can be written as (3.69 x 10^{-9}) $X_{surface}$ where $X_{surface}$ denotes the steady state mole fraction of reactive sites at the diamond surface. Similarly if a total pressure of 50 Torr is assumed then from the ideal gas law the total concentration of gas phase species is p/RT. If 1200 K is assumed as the local or substrate temperature, then the calculated total gas concentration is 6.68 x 10^{-7} mols cm^{-3}. Thus the concentration of the methyl radical, $[CH_3]$, can be written as (6.68 x 10^{-7}) X_{gas} where X_{gas} represents the mole fraction of the methyl radical local to the diamond surface. With these approximations then the growth rate can be written as:

$$\text{Growth Rate} = k \, (3.69 \times 10^{-9}) \, (6.68 \times 10^{-7}) \, X_{surface} X_{gas}$$

and to obtain an estimate of the mole fraction product of surface active sites and the methyl radical from the measured growth rate it remains to estimate the rate constant k. It is here that the remaining major assumption must be made. If it is assumed, as has been done in most modeling to date, that the diamond surface can be treated essentially as a large hydrocarbon, then k can be estimated from the measured rate constants for gas phase radical recombination reactions. For simple hydrocarbons these values range from a low of ~3 x 10^{12} cm^3 mol^{-1} sec^{-1} (for the recombination of tert-butyl radicals) to a high of ~5 x 10^{13} cm^3 mol^{-1} sec^{-1} (for addition of the methyl and ethyl radical to form n-propane) [43]. Adopting a value of 10^{13} cm^3 mol^{-1} sec^{-1} for k and changing units for the growth rate from μm hr^{-1} to mol cm^{-2} sec^{-1} gives that for a growth rate of 0.5 μm hr^{-1} (4.1 x 10^{-9} mol cm^{-2} sec^{-1}):

$$4.1 \times 10^{-9} = (10^{13}) \, (3.69 \times 10^{-9}) \, (6.68 \times 10^{-7}) \, X_{surface} X_{gas} \tag{12}$$

which reduces to:

$$X_{surface} X_{gas} = 1.6 \times 10^{-7} \tag{13}$$

The methyl radical mole fraction has recently been measured in a hot filament system and reported to be 10^{-3} to 10^{-4} [42] using a molecular beam sampling technique. From (13) this would require that the mole fraction of reactive sites at the diamond surface similarly be 10^{-4} to 10^{-3}. This is in

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reasonable agreement with an assumption that the surface concentration of reactive sites is close to its value at thermostatic equilibrium with atomic hydrogen [44]. Although this appears reasonably consistent with the hypothesis that the methyl radical is the dominant growth species, significant uncertainty remains because of the assumptions that have to be made.
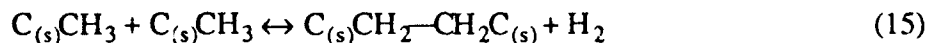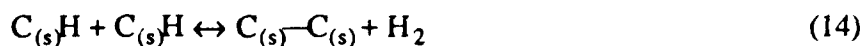
There are several possibilities for error in modeling the hot filament growth of diamond that are illustrated in part by the above calculation. Among these are that:

1. It was assumed that the addition of carbon to the growth surface is essentially an irreversible process. This can be argued reasonable in light of the large equilibrium constant expected for a radical annihilation reaction, requiring a small value for the reverse rate constant. It also appears consistent with the experimental observation that diamond is not readily gasified by atomic hydrogen. Nevertheless it remains to be established that the rate controlling step is indeed reaction (2). Given the quantitative uncertainties in such estimates, it is quite possible that the apparent agreement with experiment is more fortuitous than real.

2. No corrections were made for thermal (Soret) diffusion of the reacting species and the possibility that the growth rate is transport rather than kinetically determined was ignored.

3. It was assumed that measured gas phase rate constants for relatively simple hydrocarbons can be applied to analogous reactions at the diamond surface.

4. Most seriously, this calculation, as well as many similar modeling efforts, limits the possible reaction set to those reactions known to occur readily in gas phase hydrocarbon chemistry.

Carbon incorporation and the surface chemistry of diamond

A simple and widely accepted picture for the incorporation of carbon into the diamond lattice is a process initiated by hydrogen abstraction from an added methyl group, as seen in reaction (3). If a neighboring methyl group at the surface, or a neighboring C-H bond on the surface, is similarly converted to a radical site, then the incorporation process can be pictured as a simple radical addition. Alternatively a surface rearrangement might also be initiated by simple hydrogen metathesis as proposed by Garrison et al. [29]. These processes however are dependent upon atomic hydrogen and this raises the interesting problem of rationalizing the incorporation process for those systems where the concentration of atomic hydrogen is expected to be diminishingly small. One such case is the thermally activated growth of diamond using halocarbons, highly diluted in molecular hydrogen [45,46]. Indeed in recent work it has been reported that diamond can be grown without hydrogen present in any form [46]. The incorporation process in these experiments is obviously dependent on hydrogen, hydrogen fluoride or fluorine elimination reactions at the diamond surface which are not likely controlled by radical species. The elimination of hydrogen from the diamond surface,

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accompanied by surface reconstruction, is also known to occur at elevated temperatures (~1200 K) at very low pressures, again where metathesis by atomic hydrogen appears unlikely. These experiments suggest that the concerted addition (or elimination) of molecular hydrogen, hydrogen halides or molecular halogens, should not be ignored. Such reactions would be written as in (14), or for adjacent methyl groups, as in (15).

$$C_{(s)}H + C_{(s)}H \leftrightarrow C_{(s)}-C_{(s)} + H_2 \tag{14}$$

$$C_{(s)}CH_3 + C_{(s)}CH_3 \leftrightarrow C_{(s)}CH_2-CH_2C_{(s)} + H_2 \tag{15}$$

These represent the associative desorption (or dissociative chemisorption) of molecular hydrogen at the diamond surface and completely analogous reactions can similarly be written of course for either HF or F_2. The possibility of this type of process has largely been ignored, with most assuming that the creation and destruction of active or radical surface sites is controlled purely by reaction (3) and by:

$$C_{(s)}{}^{\bullet} + H{\bullet} \rightarrow C_{(s)}H \tag{16}$$

The reason for this is, in part, that the concerted addition or elimination of either H_2 or F_2 is forbidden by orbital symmetry constraints for simple hydrocarbon species [47]. For example a reaction such as:
$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{17}$$

is forbidden to occur as a single elementary step involving a four center transition state. The hydrogenation of ethylene (or the dehydrogenation of ethane) occurs in the gas phase by a sequence of free radical reactions, or catalytically at a solid surface. As long as the hydrogenated diamond surface is modeled simply as a large aliphatic hydrocarbon, or alternatively the dehydrogenated surface treated as a simple olefinic hydrocarbon, the same conclusion might be drawn. The difficulty with this is that the exchange reaction between H_2 and D_2 to form HD is known to be catalyzed, at temperatures too low for a gas phase radical chemistry, by an active diamond surface [48,49]. The dissociative chemisorption of H_2, and thus its reverse process, the associative desorption of H_2, D_2 or HD, is almost certainly required for this catalysis. Presumably the local symmetry at active sites on diamond is significantly different from that for simple gas phase hydrocarbons and thus constraints imposed for elementary reactions in the gas phase may not apply to the diamond surface. Clearly such a reaction may also be allowed for adjacent radical sites. Interestingly, very early modeling efforts for the dissociative chemisorption of H_2 on the surface of carbon suggested that the optimum

carbon-carbon separation for the lowest activation energy would be close to the lattice parameter of diamond, ~3.5 to 3.6 Å [50]. In addition to providing an alternative route for hydrogen elimination and carbon incorporation, this also raises the possibility that reactions and other processes, normally unexpected for simple hydrocarbons, might also occur at the growth surface. Among these might be mechanisms for the surface diffusion of carbon during growth, as methyl groups or in some other form, as well as mechanisms for the diffusion of other species, notably hydrogen, halogens, oxygen, or radical sites. If the surface diffusion of species important to a growth mechanism occurs at significant rates then many of our calculations and ideas may have to undergo substantial revision.
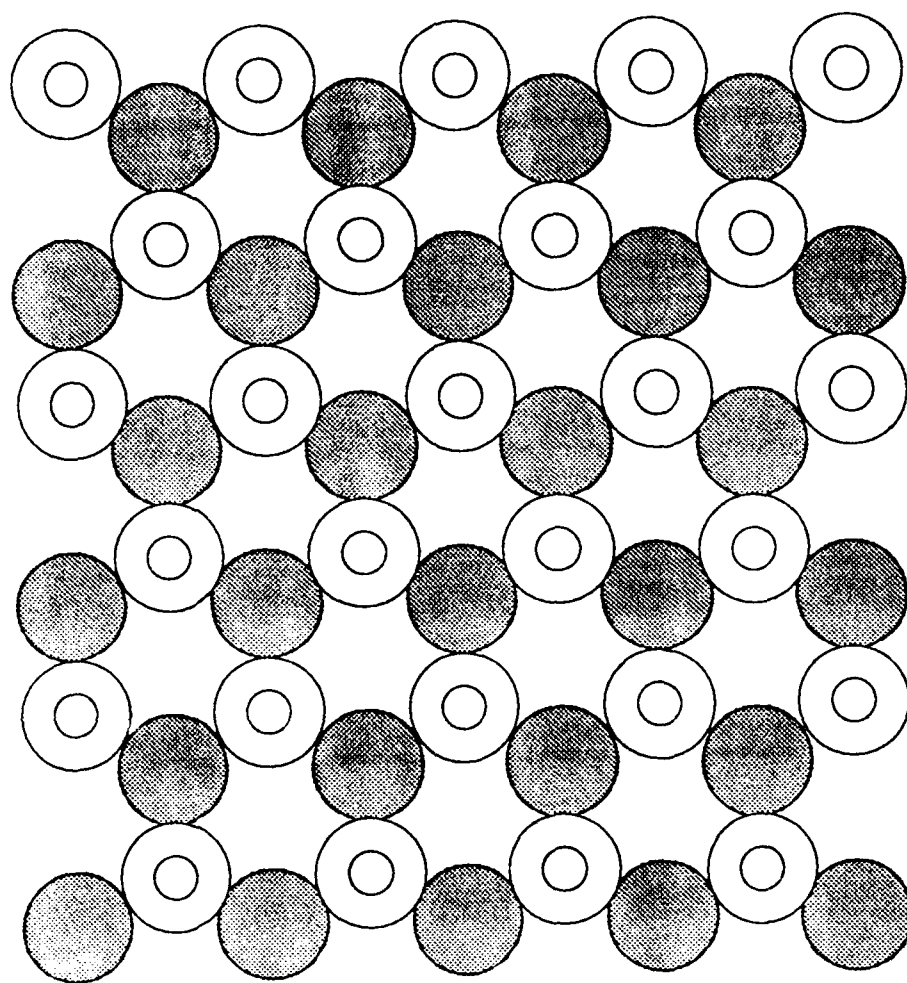
Acknowledgements

List of Figures

Figure 1

(a)

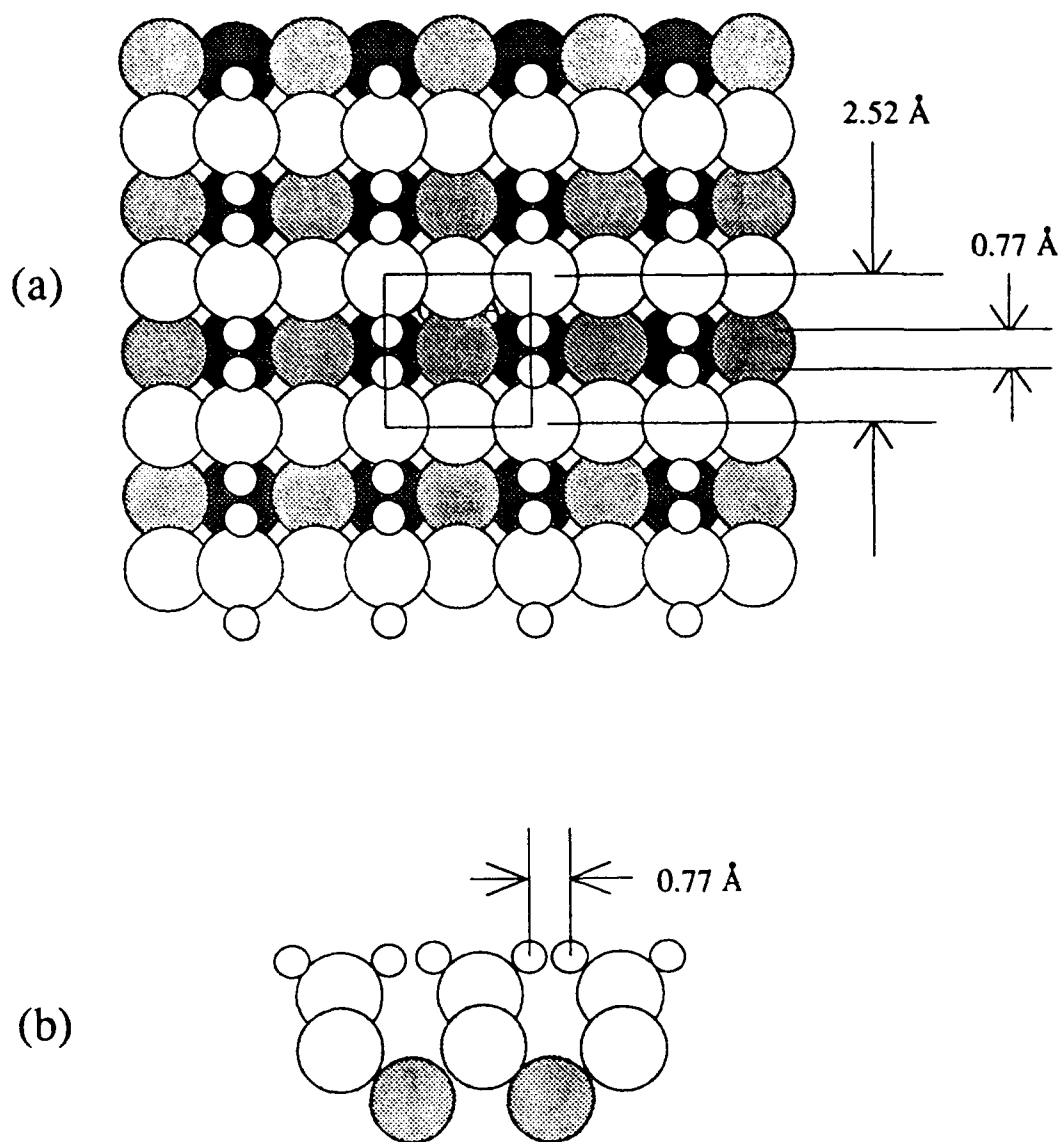2.52 Å

0.77 Å

(b)

0.77 Å

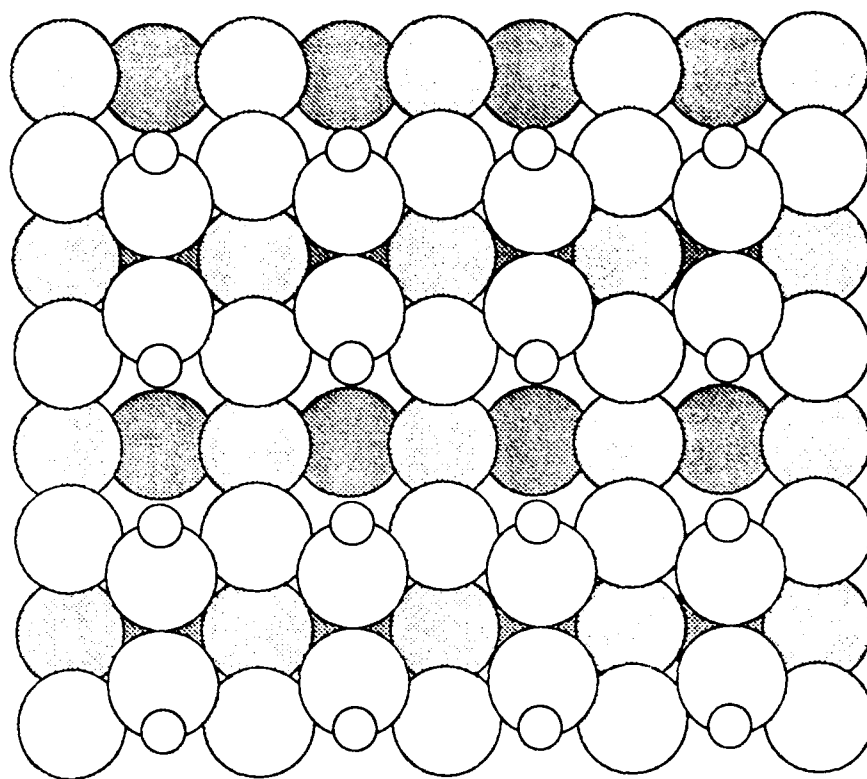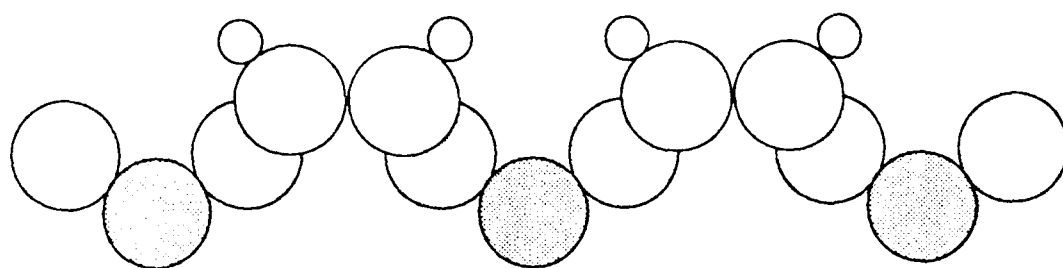Figure 2

(a)

(b)

Figure 3

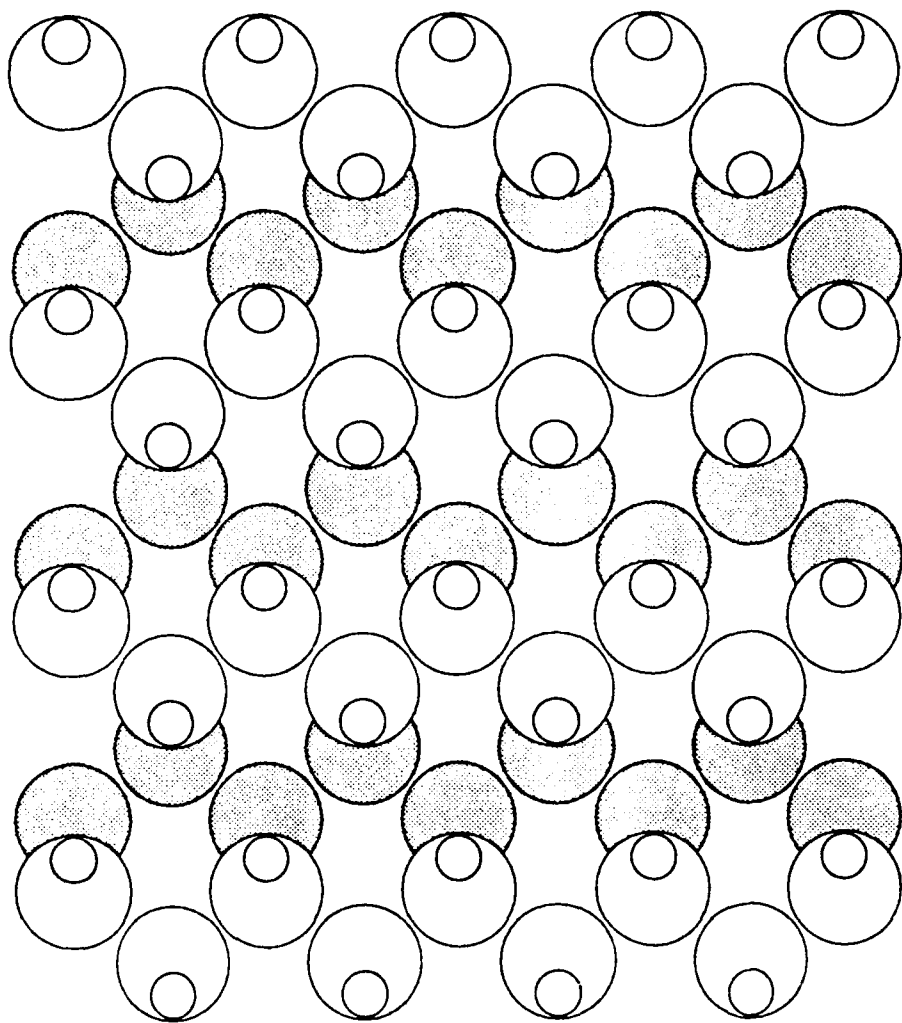Figure 4

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